



**1993 Annual Technical Report on**  
**Metastability in Molecules**  
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**Chemistry and Materials Science**

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## Overview of Prior HEDM Results

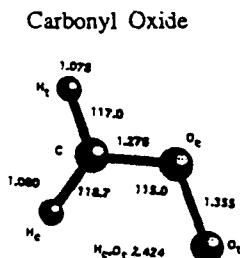
To date, the successes of our effort for the HEDM program, both methodological and in terms of metastable molecule chemistry, have been many. Considering the latter first, recognizing the prospects for highly energetic metastable species based upon nitrogen, we initiated our study of a variety of such potential molecules. These included  $N_3H_3$  [18], which is isoelectronic with the well-known species ozone, cyclopropane and propene; tetrahedral  $N_4$  [11] which is isovalent with  $P_4$  or  $As_4$ , and is forbidden by symmetry from decaying to ground state  $N_2$  molecules; octahedral  $N_8$  [11], isoelectronic with cubane and similarly forbidden from direct decomposition to  $N_2$  in its ground state; and pentazole,  $HN_5$  [10]. Each of these was found to contribute a metastable minimum on the global potential energy surface. The minima were fully characterized by calculation of the Hessian (second derivative matrix) frequently using our recently developed analytical MBPT(2) methods [14,17], which also provided the IR spectra of these unknown molecules. At this level of approximation the vibrational frequencies are normally within 5% of experiment and the relative intensities typically to within about 20% [1]. I might add, the character of a critical point on an energy surface can change depending upon whether electron correlation is included, so this is a critical test for every potential metastable molecule. Furthermore, some regard must be paid to low-lying excited states that might offer a decomposition path to ensure that the molecule is stable to unimolecular decomposition. In the absence of matrix isolation, bimolecular mechanisms can also offer ways for the target molecule to disappear.

Although sometimes postulated, there is no experimental evidence for the existence of any of these molecules. This tends to be a recurring theme in the investigation of metastable molecules. Yet, the accuracy of modern *ab initio* correlated predictions is sufficiently reliable that barring rapid bimolecular kinetics and certain possible excited state decomposition paths, the proposed metastable molecule should be capable of synthesis at least in matrix isolation and can be identified from our predicted frequencies.

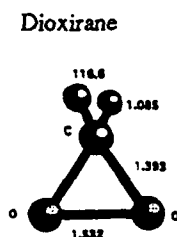
Among continued studies of nitrogen-based candidate HEDM molecules, in the last year, we have focused on characterization of transient oxidation intermediates, and the development and implementation of new theoretical methods like EOM-CC, that permit better theoretical characterization of open-shell systems and candidate atom-embedded cryogenic propellants. These topics are summarized below.

## Spectroscopic Characterization of Oxides

Synthesis and detonation of energetic materials involves several critical oxidation processes and associated intermediates. Carbonyl oxide,



and its cyclic isomeric form, dioxirane,



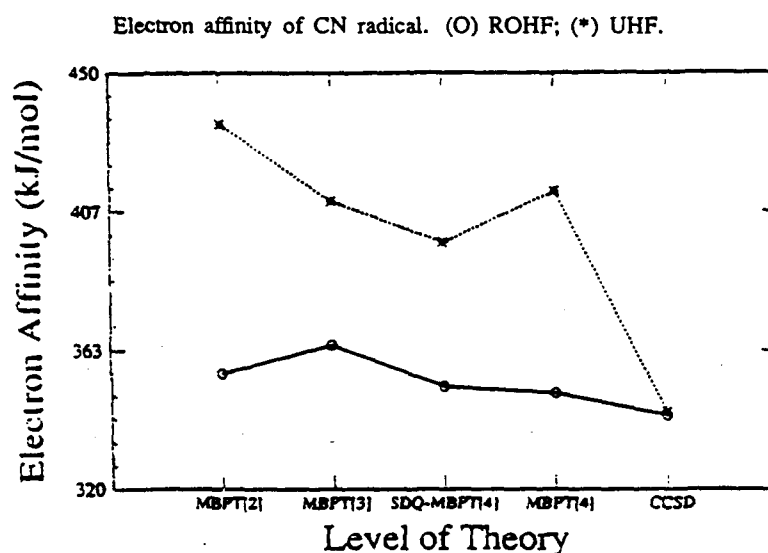
are two key compounds in such processes. Carbonyl oxide has never been observed experimentally, though it is one of the most discussed compounds awaiting detection. We performed high level coupled-cluster CCSD(T) calculations to characterize carbonyl oxide [9]. These studies employed recently developed open-shell analytical gradients methods for CCSD(T), without which structures and vibrational frequencies would be difficult to obtain. The  $\Delta H_f^\circ(298)$  for carbonyl oxide is found to be 30.2 kcal/mol, while the barrier to isomerization to dioxirane is 19.2 kcal/mol. CCSD(T) vibrational frequencies of both species are presented to facilitate identification along with the  $^{18}\text{O}$  isotope shifts. Shifts as high as  $45\text{cm}^{-1}$  permit experimental discrimination between the two forms. Carbonyl oxide is found to be far more zwitterionic than lower level theoretical studies would suggest, in line with the viewpoint of synthetic chemists.

## Methodological Advances

The ability to provide accurate energetic and spectroscopic results for candidate HEDM molecules rests upon new developments in *ab initio*, electronic structure theory. Several such advances have been accomplished in the last period of this grant. All are incorporated into the ACES II program system which is now widely used throughout the world, including industry (Lubrizol, Dupont, Ford, etc.) and other government agencies (NASA Ames, DOE's Battelle, Pacific Northwest Laboratory, etc.).

1. Open shell molecules are frequently more difficult to describe accurately than those where all electrons are paired. The most widely used procedure for open shells is to start with an unrestricted Hartree Fock (UHF) reference and add electron correlation via MBPT (also

known as MP) theory. However, for many problems, UHF solutions suffer from spin-contamination as the UHF function is not an eigenfunction of spin. For some problems, a restricted open shell Hartree Fock (ROHF) reference, which is a spin eigenfunction, is a better choice. However, because the ROHF method uses different Fock operators in its determination, one for doubly orbital orbitals, and one for singly occupied orbitals, it was not clear how to use an ROHF reference in MBPT calculations. We solved this problem to provide a non-iterative ROHF-MBPT method for second, third and fourth order [17], that is no more expensive than the usual UHF-MBPT calculations, but one that offers vastly better convergence to the exact result for spin contaminated cases. This is illustrated in Fig. 1 for the CN radical.



Note that at the ROHF-MBPT(2) level, there is good agreement with infinite order CCSD results, while UHF-MBPT(2) is far from the converged answer. Furthermore, finite order MBPT failed to rectify this failing of the UHF, spin contaminated reference.

2. To locate critical points on an energy surface,  $E(R)$ , as minima or transition states, requires the facile evaluation of the forces on the atoms in a molecule,  $\nabla E(R)$ . Since molecules have  $3N-6$  degrees of freedom where  $N$  is the number of atoms, repeated calculation of  $E(R)$  in all degrees of freedom is a hopeless procedure for most polyatomic molecules. However, by also evaluating  $\nabla E(R)$  *analytically*, in about the same time as  $E(R)$  itself, it is comparatively easy to locate the minimum energy geometry where the atomic forces vanish. We provided the initial ROHF-MBPT(2) analytical gradients under this grant [14], and used it in several applications to transient molecules like FCS.
3. The other primary methodological advance achieved last year is the general formulation and implementation of the equation-of-motion (EOM-CCSD) method for excited states, UV-visible spectra, and associated properties. This is a very general method that shows promise of being the method of choice for excited states. The theory [1,5,6] and several applications

[4-6,8] have been recently reported.

The basic idea of EOM-CC is that most of the dynamical correlation in a ground (or reference) state is quite similar to that in an excited, ionized, or electron attached state; but the non-dynamical correlation is quite different, and any suitable method must account for this difference.

Consider the Schrödinger equation for the general single state and  $k$ th excited state:

$$H\psi_o = E_o\psi_o$$

$$H\psi_k = E_k\psi_k$$

where  $\psi_k = R_k\psi_o$ , we have

$$HR_k\psi_o = E_k R_k\psi_o$$

$$R_k H\psi_o = E_o R_k\psi_o$$

$$\text{or, } [H, R_k]\psi_o = (E_k - E_o)R_k\psi_o = \omega_{ko} R_k\psi_o$$

By choosing  $\psi_o = \exp(T)\Phi_o$ , the CC choice, we obtain

$$[e^{-T} H e^T, R_k]\Phi_o = \omega_{ko} R_k\Phi_o$$

$$[\bar{H}, R_k]\Phi_o = \omega_{ko} R_k\Phi_o$$

$$(\bar{H} R_k)_c \Phi_o = \omega_{ko} R_k\Phi_o$$

In matrix form, we have

$$\bar{H} R_k = R_k \omega_{ko}$$

A particularly appropriate application of EOM will be to study the spectroscopic signatures of atoms and molecules embedded in cryogenic matrices. Species proposed include the Li, Be, B, Mg and Al atoms. Furthermore, atom migration will lead to diatomic molecule formation and, eventually clusters. These, too, will contribute to the spectroscopic signature. Results are shown in Tables 1-5 for the five atoms, while Figure 1 shows B<sub>2</sub> triplet excited state curves. Table 6 is an example for the molecule Acetaldehyde. The high accuracy of EOM-CCSD for these systems is apparent. Other comparisons are made to the single reference CCSD and Fock Space (FS-CC) results.

Table 1: Li Atom Excitation Energies.

<i>State</i>	<i>Main Excitation</i>	<i>EE-EOMCC (Li)</i>	<i>Exp.</i>
$2p^0$	$2s \rightarrow 2p$	1.85	1.85
$2S$	$2s \rightarrow 3s$	3.37	3.37
$2p^0$	$2s \rightarrow 3p$	3.83	3.83
$2D$	$2s \rightarrow 3d$	3.96	3.88
	$\Delta\text{CCSD}$	IP-EOMCC	Exp.
First IP	5.38	5.38	5.39

Table 2: B Atom Excitation Energies. The EE-EOMCC results are relative to the  $1s^2 2s^2 3s$  state ( $B^*$ ) of B.

<i>State</i>	<i>Main Excitation</i>	<i>EE-EOMCC (<math>B^*</math>)</i>	<i>Exp.</i>	<i>FSCC(1,2)</i>
$4p$	$2s \rightarrow 2p$	—	3.57	3.70
$2S$	$2p \rightarrow 3s$	4.96	4.96	—
$2D$	$2s \rightarrow 2p$	—	5.93	6.10
$2p^0$	$2p \rightarrow 3p$	5.99	—	—
$2D$	$2p \rightarrow 3d$	6.65	6.79	—
	$\Delta\text{CCSD}$		Exp.	
First IP		8.20	8.30	

Table 3a: Be excitation spectrum: Singlet states

<i>State</i>	<i>EE-EOMCC</i>	<i>Exp.</i>
2s2p $^1P^0$	5.282	5.277
2s3s $^1S$	6.812	6.779
2p <sup>2</sup> $^1D$	7.225	7.050
2s3p $^1P^0$	7.484	7.462
2s3d/2p <sup>2</sup> $^1D$	9.778	7.988

Table 3b: Be excitation spectrum: Triplet states

<i>State</i>	<i>EE-EOMCC</i>	<i>Exp.</i>
2s2p $^3P^0$	2.706	2.725
2s3s $^3S$	6.460	6.457
2s3p $^3P^0$	7.316	7.303
2p <sup>2</sup> $^3D$	—	7.401
2s3d $^3D$	8.810	7.694

Table 4a: Mg excitation spectrum: Singlet states

<i>State</i>	<i>EE-EOMCC</i>	<i>Exp.</i>
3s3p $^1P^0$	4.354	4.346
3s4s $^1S$	5.444	5.394
3s3d/3p <sup>2</sup> $^1D$	5.973	5.753
3s4p $^1P^0$	7.179	6.118
3p <sup>2</sup> /3s3d $^1D$	8.138	6.588

Table 4b: Mg excitation spectrum: Triplet states

<i>State</i>	<i>EE-EOMCC</i>	<i>Exp.</i>
3s3p $^3P^0$	2.672	2.712
3s4s $^3S$	5.104	5.108
3s3d $^3D$	6.342	5.946
3s4p $^3P^0$	6.742	5.932



Table 5: Al Atom Excitation Energies. Reference is  $\text{Al}^*$ , the  $1s^2 2s^2 2p^6 3s^2 4s$  state of Al.

<i>State</i>	<i>Main Excitation</i>	<i>EE-EOMCC (<math>\text{Al}^*</math>)</i>	<i>Exp.</i>	<i>FSCC (1,2)</i>
$^2\text{S}$	$3p \rightarrow 4s$	3.17	3.14	—
$^4\text{P}$	$3s \rightarrow 3p$	—	3.60	3.66
$^2\text{D}$	$3p \rightarrow 3d$ $3s \rightarrow 3p$	4.18	4.02	4.46
$^2\text{P}^0$	$3p \rightarrow 4p$	4.09	4.09	—
		$\Delta\text{CCSD}$	Exp.	
First IP		5.91	5.98	

# B2 Excited State Pot. Curves

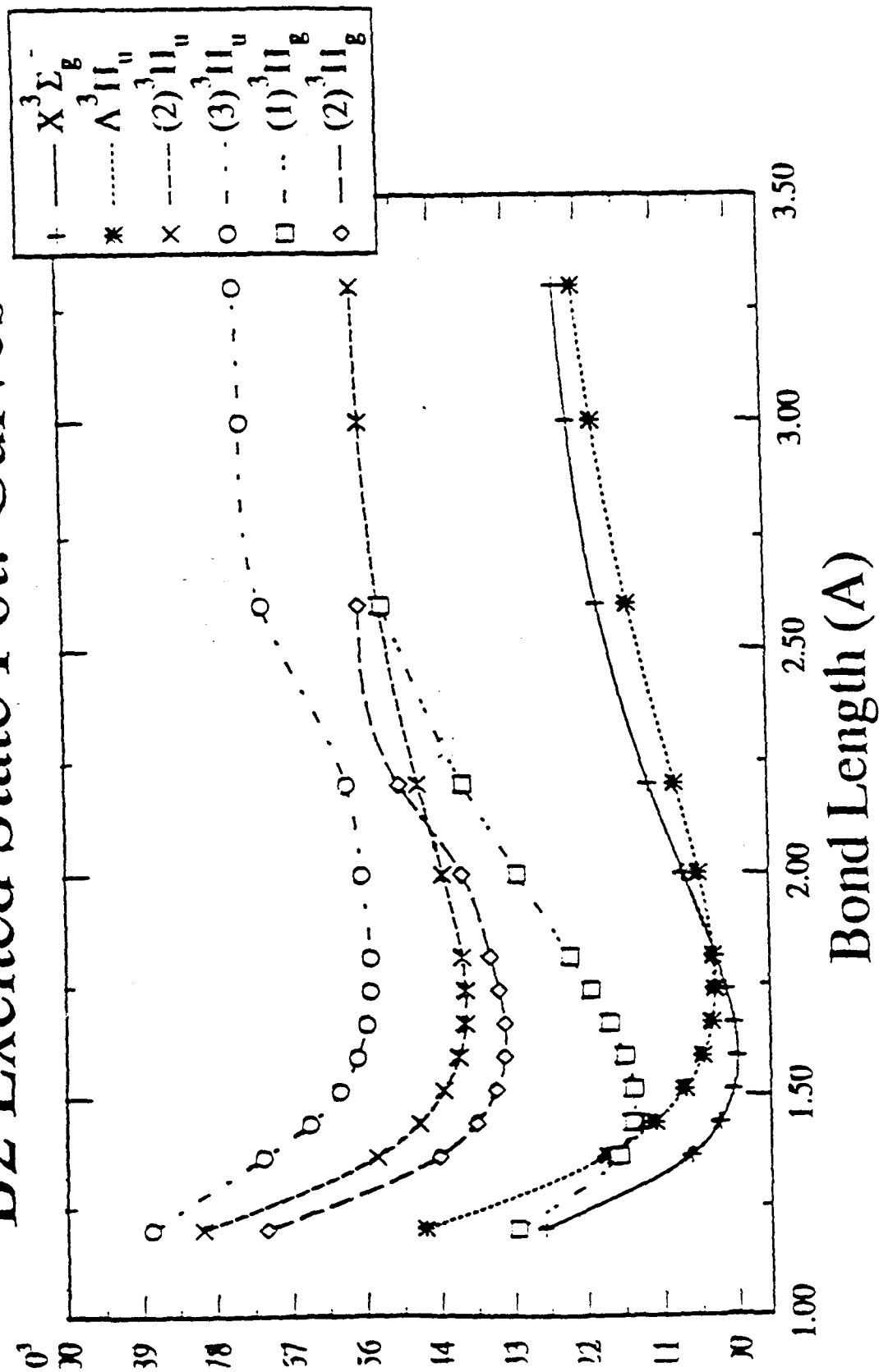


Table 6: Acetaldehyde

state	EOM-CC	expt	osc. str.	AEL
1 <sup>1</sup> A'' (valence)	4.32	4.28	6x10 <sup>-5</sup>	1.08
2 <sup>1</sup> A' (3s)	6.79	6.82	0.015	1.08
3 <sup>1</sup> A' (3p)	7.47	7.46	0.075	1.08
2 <sup>1</sup> A'' (3p)	7.75		0.011	1.08
4 <sup>1</sup> A' (3p)	7.80	7.75	0.020	1.08
5 <sup>1</sup> A' (3d)	8.54	8.43	0.014	1.08
6 <sup>1</sup> A' (3d)	8.75	8.69	0.055	1.08
3 <sup>1</sup> A'' (3d)	8.90		8x10 <sup>-5</sup>	1.08
4 <sup>1</sup> A'' (3d)	9.07		0.024	1.08
7 <sup>1</sup> A' (3d)	9.11		0.005	1.08
5 <sup>1</sup> A'' (valence)	9.28		5x10 <sup>-5</sup>	1.08
8 <sup>1</sup> A' (valence)	9.43		0.210	1.08

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